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Self passivating W-based alloys as plasma-facing material

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ABSTRACT

Self passivating tungsten-based alloys may provide a major safety advantage in comparison with pure tungsten (W) which is presently the main candidate material for the plasma-facing protection of future fusion power reactors. Films of binary and ternary tungsten alloys were synthesised by magnetron sputtering. The oxidation behaviour was measured with a thermobalance set-up under synthetic air at temperatures up to 1273 K. Binary alloys of W–Si showed good self-passivation properties by forming a SiO_2 film at the surface. Using the ternary alloys W–Si–Cr, W–Si–Y, and W–Si–Zr the oxidation behaviour could be further improved.

1. Introduction

Compared with other materials, tungsten (W) has the advantage of very low sputter erosion under bombardment by energetic D, T, He ions and atoms from the plasma. Thus a W-based protection material may provide a wall erosion lifetime of the order of five years which is a pre-requisite for economic fusion reactor operation [1–3].

A potential problem with the use of pure W in a fusion reactor is the formation of radioactive and highly volatile WO_3 compounds and their potential release under accidental conditions.

A loss-of-coolant accident (LOCA) in a He-cooled reactor would lead to a temperature rise to 1373 K after ~10–30 days due to the nuclear decay heat of the in-vessel components [1]. In such a situation additional accidental intense air ingress into the reactor vessel would lead to the formation of WO_3 and subsequent evaporation of radioactive $(WO_3)_x$-clusters [4,5]. The use of self passivating W alloys either as bulk material or as thick coating on the steel wall may be an alternative and passively safe approach for plasma-facing protection. The use of this material would eliminate the above mentioned concern related to pure W.

A future application of binary or ternary tungsten-based alloys in a fusion reactor appears feasible, since these compounds can also be processed to thick protective coatings with reasonable thermal conductivity, e.g. by plasma spraying with subsequent densification. Enhanced sputter erosion during normal reactor operation due to the Si and Cr addition is not a concern, since preferential sputtering of alloying elements like Si and Cr will lead to rapid depletion of the first atomic layers and leave a pure W-surface in contact with the plasma [6].

Important is the behaviour of the alloying elements regarding neutron irradiation. Since the induced radioactivity after 100 years must be below the "Hands on" level, promising oxide formers like Ni or Al are inapplicable for fusion energy. Therefore other alloying elements which form stable oxides with low partial pressure at high temperatures have to be identified. In this paper the oxidation and self-passivation behaviour of ternary tungsten-based alloys applying the alloying elements Si, Zr, Cr, Y is investigated.

2. Experimental

Thin W–Si–Zr, W–Si–Y, and W–Si–Cr coatings were synthesized and subjected to oxidation at high temperatures to study the self-passivation of the W alloys in comparison to pure W. For this study coatings with μm thickness have been used, because alloys of different composition could be easily deposited using a commercial magnetron sputtering facility. The films are used as model for the oxidation behaviour of bulk materials. The sputter deposition leads to a nanoscale distribution of all elements of the alloy which may be important regarding the diffusion behaviour of the species.

As an addition to a former study, described in detail in [7], which used two magnetrons, the ternary tungsten alloys of the present study have been deposited using a deposition set-up equipped with three magnetrons. This enabled co-deposition of three components with arbitrary composition. The sputter targets were made of pure W (99.5 wt.%), Si (99.999%), Cr (99.95%), Y (99.5%), and Zr (99.9%), partially produced by powder metallurgy. Quartz and alumina substrates have been used, which are fully oxidation resistant and which do not react with the W alloys over the investigated temperature range. The deposition parameters for the ternary alloys are shown in Table 1.

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Table 1
Sputter deposition parameter for ternary tungsten alloy films. Target diameter: 7.5 cm, Ar pressure: 1.2 Pa. The name of the alloy shows the composition of alloying elements in weight percent. Compositions measured by ion beam analysis.

Film	Targets, power [W]					Composition [at.%]				
	W	Si	Cr	Zr	Y	W	Si	Cr	Zr	Y
WSi13Zr13	145	368		46		40	46		14	
WSi12Cr7	145	368	30			44	42	14		
WSi8Cr12	209	401	76			45	30	25		
WSi9Y13	210	400			100	47	36			17

3. Results

3.1. As deposited coatings

The composition of the coatings was measured by Rutherford backscattering (RBS) analyses on thin coatings (300 nm) deposited on graphite substrates. The results were used to estimate the composition of the thicker coatings (3–5 μm) deposited with the identical parameter set on quartz and alumina substrates. The results of the RBS measurements are shown in Table 1. The density values of the films were close to theoretical densities assuming no formation of other crystalline phases.

XRD analysis (X-ray diffraction) of the as deposited films showed for all alloys very broad reflexes, corresponding to a small crystallite size of tungsten. Reflexes of the alloying elements Si, Cr, Zr, and Y or their compounds have not been observed on as deposited samples. Fig. 1 shows the XRD spectrum of a WSi12Cr7 film, deposited on alumina.

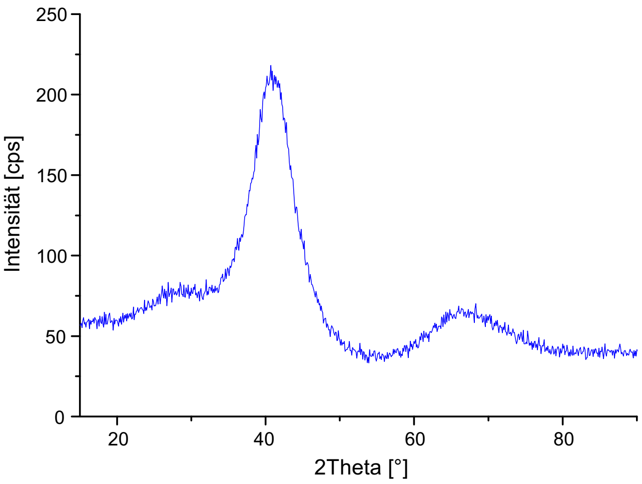

Fig. 1. XRD measurements of WSi12Cr7 film, as deposited.

The low degree of crystallinity is similar to the reported results on tungsten alloys, containing silicon with a comparable amount [7]. The examination using scanning electron microscopy (SEM) confirms the XRD results and shows a very smooth structure without any details.

3.2. Oxidation test results

The tungsten alloy films have been oxidized at 873, 1073, and 1273 K with synthetic air at atmospheric pressure. The mass gain of the samples due to the formation of the metal oxides has been measured using a thermobalance set-up.

3.2.1. W–Si alloys

The results of the binary W–Si alloys are reported in detail in [7]. It has been shown that the additions of silicon to tungsten lead to the formation of a protective and dense SiO_2 layer at the outer surface. The oxidation rate of W–Si alloys depends on the content of Si. Increasing Si content decreases the oxidation rate. SEM images (Fig. 2) show a sample of W–13 wt.% Si after oxidation at 1073 K for 4 h. The conversion of Si to SiO_2 and of W to WO_3 was not completed after that time. The light grey areas of Fig. 2(a) have an oxygen content of 12 at.% according to EDX (energy dispersive X-ray) analysis. Taking the sampling depth of the EDX analysis into account (order of a μm), we interpret the light grey area as the domain of the sample where the alloy is protected by a thin film of SiO_2. By contrast the oxygen content of the dark areas is about 62 at.%, which we interpret as follows: with increasing oxidation time the SiO_2 scale grows and the content of Si in the W-based alloy layer becomes lower, W starts to oxidize with a resultant strong increase of volume. This may locally damage the protecting SiO_2 layer. The full oxidation of W starts at this nucleation site, the totally oxidized areas grow radially from this nucleation site. This formed the dark circles which have been grown together, Fig. 2(a). They cover a large part of the surface. Fig. 2(b) shows the marked detail of the surface of Fig. 2(a) demonstrating the volume increase of the strongly oxidized zones. The thickness of this zone is in the order of the information depth of the EDX analysis. Therefore the oxygen content of this area reflects the nearly complete conversion of W and Si to their oxides. A possible origin of such nucleation sites for increased oxidation may be microscopic voids in the 3coating e.g. pinholes, embedded micro particles or substrate inhomogeneities.

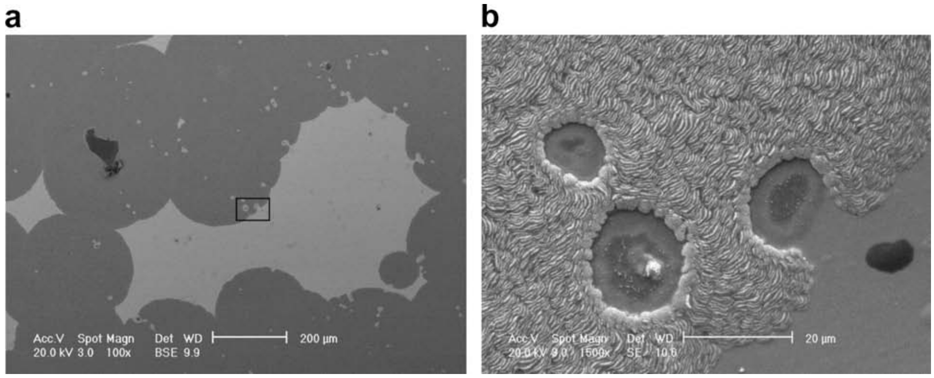

Fig. 2. SEM plan view of 1 μm WSi13 oxidized at 1073 K for 4 h. The light grey areas of image (a) have a low oxygen content according to EDX analysis. The oxygen content of the dark area is about 62 at.%. Image (b) shows the marked detail of the left.

Table 2
Linear oxidation rates of ternary tungsten alloys.

	Linear oxidation rate/mg cm^{-2} s^{-1}		
	873 K	1073 K	1273 K
WSi13*	1.0×10^{-5}	3.1×10^{-4}	2.3×10^{-3}
WSi13Zr13	2.5×10^{-6}	5.0×10^{-5}	6.3×10^{-4}
WSi12Cr7	2.3×10^{-7}		5.0×10^{-6}
WSi8Cr12	5.7×10^{-7}	7.1×10^{-6}	5.4×10^{-5}
WSi9Y13	8.5×10^{-7}	1.4×10^{-5}	2.2×10^{-4}

* The values for the oxidation rates of WSi13 are taken from Ref. [7].

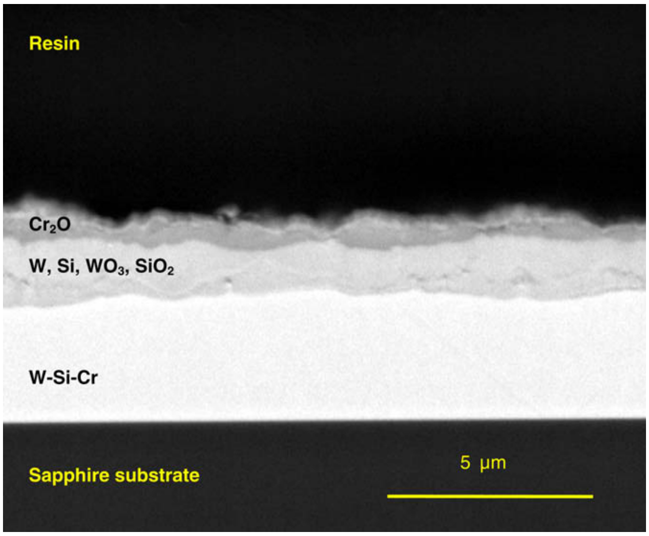

Fig. 3. SEM cross sectional view of WSi12Cr7, oxidized at 1273 K for 1 h.

3.2.2. Ternary tungsten alloys

SEM observations of the plane surface of oxidized ternary alloys show similar characteristics like W–Si. At first a protective oxide scale will be formed. With increasing time also the growth of thicker oxide structures in radial directions have been observed. But, depending on the composition, the addition of a third component led to a considerable enhancement of the self-passivation properties. Table 2 shows the oxidation rates *k* of the investigated ternary alloys, obtained by linear fitting of the mass changes during the initial part of oxidation. As reference, the oxidation rates for a binary WSi13 from Ref. [7] have been inserted. Whereas the reduction of the velocity of oxidation was small in case of Zr addition, despite of the relatively high degree of alloying, Cr and Y additions at lower concentration led to higher oxidation resistance. The respective Arrhenius plots are given in Fig. 4.

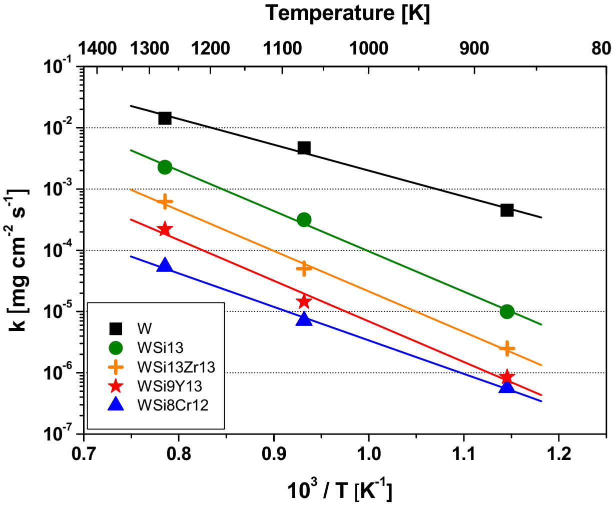

Fig. 4. Arrhenius plot of oxidation rates of pure tungsten, WSi13, WSi13Zr13, WSi9Y13, and WSi8Cr12.

Si was identified to be an essential component of ternary alloys. Oxidation experiments of binary and ternary alloys without Si often showed dramatic failures which led to the total delamination of the coatings from the substrate. Apparently the SiO_2 did not form the surface permeation barrier in the investigated temperature range. This oxide barrier scale at the outer surface was formed always by the oxide of the third alloying element of the compound. Below the outer oxide scale a closed and dense SiO_2 scale was not identified. Instead, rather a Si/W zone containing some Si- and W-oxide was formed. In this zone Si inhibited the fast oxidation of W. Fig. 3, a SEM cross sectional view of a WSi12Cr7 film, oxidized at 1273 K for 1 h, shows this structure. Below the barrier scale of Cr_2O_3, a zone without Cr has been formed, containing W, Si, and their oxides WO_3 and SiO_2. The formation of a mixed W-Si zone during oxidation of ternary alloys is the reason of the higher performance compared to binary W–Si alloys where the depletion of Si below the SiO_2 barrier scale lead to a zone of unprotected tungsten.

At low temperatures the performance of the films with Y additions was of the same order like those with Cr additions. With increasing temperature the Cr containing alloy showed a better performance. Therefore for an application as plasma-facing material the system W–Si–Cr could be used to reduce the accidental evaporation of radioactive WO_3 in a future fusion power plant.

4. Conclusion

The self-passivation mechanism of substoichiometric W–Si compounds and of ternary tungsten-based alloys under oxidation has been shown. The addition of Si and Cr has been found to lead to the best self-passivation behaviour under air exposure up to 1000 °C.

In case of an accidental temperature rise under LOCA conditions the diffusion of Si and Cr in W will lead to the enrichment of oxide scale forming elements at the surface which is needed for the formation of a passivating dense oxide layer.

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